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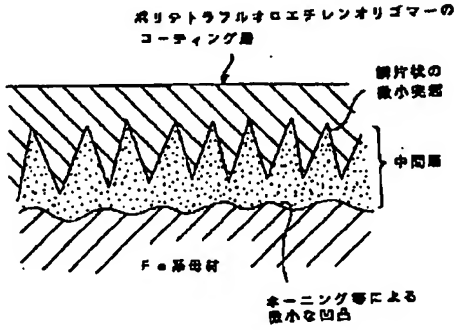
(54) LAMINATED BODY HAVING COATING LAYER AND ITS MANUFACTURE

(57) Abstract:

PURPOSE: To firmly fix a polytetrafluoroethylene oligomer which is superior in mold release properties and sliding properties on the surface of a base material and performed at equipment saving state and low cost.

CONSTITUTION: A laminated body is provided with an intermediate layer comprised of an Fe base material and a compound between Fe-Al metalls or a phosphoric zinc coating having a large number of scalelike minute protrusions and a coating layer comprised of polytetrafluoroethylene oligomer encroaching upon scale structure of the intermediate layer under a state wherein the intermediate layer is coated with the coating layer. At the time of formation of the coating layer comprised of the polytetrafluoroethylene oligomer, after powdery body of the polytetrafluoroethylene oligomer is stuck on the intermediate layer of the scale structure, stoving of the polytetrafluoroethylene oligomer is performed by heating.



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CLAIMS

[Claim(s)]
[Claim 1] The base material which consisted of a metal which uses Fe as a main component, and was fabricated by the predetermined configuration, the interlayer who has the minute projection of a majority of shape of a scale which formed the bonnet, and Fe component and the intermetallic compound of a base material for a part of this base material [at least], or a pole -- the formation which has the minute projection of a detailed schuppen structure -- with the interlayer who consists of a coat The layered product which has the coating layer characterized by providing the layer of the polytetrafluoroethylene oligomer fixed to the above-mentioned minute projection in the above-mentioned interlayer in the condition of having entered between the above-mentioned minute projections of the interlayer of a bonnet parenthesis.
[Claim 2] The layered product in which the above-mentioned middle class has the coating layer according to claim 1 which is a Fe-aluminum intermetallic compound.
[Claim 3] the above-mentioned interlayer -- formation of either a phosphoric-acid zinc coat or a phosphoric-acid manganese coat -- the layered product which has the coating layer according to claim 1 which is a coat.
[Claim 4] The process which forms in a base material front face the minute projection of a majority of shape of a scale which consists of a Fe-aluminum intermetallic compound by immersing the part which should carry out coating of the base material which uses Fe as a main component into melting aluminum, The process which makes the fine particles of polytetrafluoroethylene oligomer adhere to the above-mentioned minute projection, The manufacture approach of the layered product which has the coating layer characterized by providing the process which is made to carry out melting of the fine particles of the above-mentioned polytetrafluoroethylene oligomer, and is baked on the above-mentioned minute projection by heating to the temperature more than the melting temperature of polytetrafluoroethylene oligomer.
[Claim 5] The process which forms the minute projection of a majority of shape of a scale which heats a base material in a vacuum or inert gas at the temperature of 500 degrees C - 1000 degrees C, and becomes a base material front face from a Fe-aluminum intermetallic compound after making aluminum vapor-deposit the part which should carry out coating of the base material which uses Fe as a main component by sputtering, The process which makes the fine particles of polytetrafluoroethylene oligomer adhere to the above-mentioned minute projection, The manufacture approach of the layered product which has the coating layer characterized by providing the process which is made to carry out melting of the fine particles of the above-mentioned polytetrafluoroethylene oligomer, and is baked on the above-mentioned minute projection by heating to the temperature more than the melting temperature of polytetrafluoroethylene oligomer.
[Claim 6] The process which forms the minute projection of a majority of shape of a scale which consists of a coat of phosphoric-acid zinc or phosphoric-acid manganese by chemical conversion in the front face of the part which should carry out coating of the base material which uses Fe as a main component, The process which makes the fine particles of polytetrafluoroethylene oligomer adhere to

the above-mentioned minute projection, The manufacture approach of the layered product which has the coating layer characterized by providing the process which is made to carry out melting of the fine particles of the above-mentioned polytetrafluoroethylene oligomer, and is baked on the above-mentioned minute projection by heating to the temperature more than the melting temperature of polytetrafluoroethylene oligomer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the layered product which has a coating layer suitable for the components with which the property which crawls liquids, such as what a mold-release characteristic is required as like the molding die of for example, a synthetic-resin product, and water repellence, oil repellency, is demanded, or the moving part as which low friction, abrasion resistance, etc. are required like a dry bearing, and its manufacture approach.
[0002]
[Description of the Prior Art] A good mold-release characteristic is required so that a product can separate the molding die of a synthetic-resin product from a metal mold inner surface smoothly at the time of product drawing after shaping. In the metal mold for fabricating the resin which has an adhesive property like urethane resin or an epoxy resin especially, in order to avoid that resin pastes a metal mold inner surface, the release agent is applied to the metal mold inner surface.
[0003] Since the usual wax used as a release agent has good wettability with resin, a wax will separate from a metal mold inner surface at the time of mold release. Therefore, it is necessary to newly [whenever it fabricates a resin product once] apply a wax to a metal mold inner surface, and it has been a problem conventionally that the cost of a wax becomes a large sum considerably or to become the cause of worsening work environment.
[0004] On the other hand, if a wettability small wax with resin is applied to a metal mold inner surface, it can leave a wax to a metal mold inner surface at the time of mold release. However, with a wax without thermal resistance, even if it uses such a wax, since it deteriorates with heating at the time of resin shaping, there is a problem that the original mold-release characteristic is unmaintainable over a long period of time.
[0005] Moreover, by carrying out baking finish of the polytetrafluoroethylene it is supposed that there is a mold-release characteristic to components, such as metal mold, a mold-release characteristic is given or lowering coefficient of friction is also performed. However, since a mold-release's characteristic not being so good and the mechanical strength of polytetrafluoroethylene are comparatively low, it wears out throughout [activity term], and there is a limitation in a prolonged activity.
[0006] Moreover, low-molecular-weight polytetrafluoroethylene (TFEO), i.e., polytetrafluoroethylene oligomer, is known as the mold-release characteristic superior to polytetrafluoroethylene, and an ingredient in which low coefficient of friction is shown. However, neither polytetrafluoroethylene oligomer's having a mechanical strength still smaller than the usual polytetrafluoroethylene for low molecular weight nor a practical means for it to be stabilized and to fix to other material-list sides since wettability with other ingredients is remarkable and bad because of the small surface energy is established. For this reason, the actual condition is that neither the outstanding mold-release characteristic which polytetrafluoroethylene oligomer has, nor sliding nature is harnessed.
[0007] Moreover, using the composite-coatings liquid which distributed the polytetrafluoroethylene oligomer particle, a processed material is galvanized and forming the composite-coatings coat in which

the polytetrafluoroethylene oligomer particle carried out eutectoid distribution on a processed material is also proposed as indicated by JP,4-285199,A.

[0008]

[Problem(s) to be Solved by the Invention] When forming the composite-coatings coat which carried out eutectoid distribution of the above polytetrafluoroethylene oligomer particles, in the case of the comparatively big metal mold used in order to fabricate large-sized resin components like the sheet pad for FRP flat spring Sagitta seats of an automobile for suspension, it needs a quite big plating tub, and a facility not only becomes large-scale, but attaches the cost of plating liquid highly. Moreover, it is hard to form a uniform coat in the components of a complicated configuration. and in order to use plating liquid, exceptional consideration is required for work environment -- etc. -- when attaining utilization, there is a difficult problem.

[0009] Therefore, the object of this invention can fix firmly the coating layer of polytetrafluoroethylene oligomer with the property excellent in a mold-release characteristic, sliding nature, etc. to a base material front face, and moreover, its large-sized facility like a plating tub is unnecessary, and it is to offer the layered product which can be carried out by low cost, and its manufacture approach.

[0010]

[Means for Solving the Problem] The layered product of this invention developed in order to achieve the above-mentioned object The base material which consisted of a metal which uses Fe as a main component, and was fabricated by the predetermined configuration as typically shown in drawing 1 , the interlayer who has the minute projection of a majority of shape of a scale which formed the bonnet, and Fe component and the intermetallic compound of a base material for a part of this base material [at least], or a pole -- the formation which has the minute projection of a detailed schuppen structure -- with the interlayer who consists of a coat It is characterized by providing the layer of the polytetrafluoroethylene oligomer fixed to the above-mentioned minute projection in the above-mentioned interlayer in the condition of having entered between the above-mentioned minute projections of the interlayer of a bonnet parenthesis.

[0011] The molecular weight of polytetrafluoroethylene oligomer is 10000 or less. the above-mentioned interlayer -- for example, formation of a Fe-aluminum intermetallic compound, a phosphoric-acid zinc coat, or a phosphoric-acid manganese coat -- it is a coat.

[0012] Although the above-mentioned coating layer (the middle class and layer of polytetrafluoroethylene oligomer) may be prepared in the whole base material, if it prepares only in the part which usually needs coating like a metal mold inner surface, it is sufficient for it.

[0013] The manufacture approach of this invention possesses the process which is made to carry out melting of the fine particles of the above-mentioned polytetrafluoroethylene oligomer, and bakes on the above-mentioned minute projection by heating to the process which forms the middle class who becomes the part which should carry out coating of the base material which uses Fe as a main component from the minute projection of the shape of a majority of scale, the process which makes the fine particles of polytetrafluoroethylene oligomer adhere to the above-mentioned minute projection, and the temperature more than the melting temperature of polytetrafluoroethylene oligomer.

[0014] The approach of forming in a base material front face the minute projection of a majority of shape of a scale which consists of a Fe-aluminum intermetallic compound, when the process which forms the above-mentioned interlayer is immersed in melting aluminum in a base material, How to form the minute projection of a majority of shape of a scale which heats a base material in a vacuum or inert gas at the temperature of 500 degrees C - 1000 degrees C, and becomes a base material front face from a Fe-aluminum intermetallic compound after making aluminum vapor-deposit by sputtering, Or the approach of forming in a base material front face the minute projection of a majority of shape of a scale which consists of a coat of phosphoric-acid zinc or phosphoric-acid manganese by chemical conversion is adopted.

[0015]

[Function] As the coating layer of this invention eats into the interlayer which polytetrafluoroethylene oligomer becomes from the minute projection of the shape of much scale, it is being firmly fixed to the

base material front face, and it excels in abrasion resistance, and a mechanical strength is size. the intermetallic compound which constitutes an interlayer, or formation -- a coat is hard and, moreover, its bond strength with a base material is very large.

[0016] If the surface area of a base material is made to increase by preparing minute irregularity by honing etc. on the surface of the base material beforehand before forming the above-mentioned interlayer, association with a base material and an interlayer will become still firmer.

[0017] Since the middle class who is the aggregate of a minute scale-like projection has very large surface area, he can achieve the duty which holds polytetrafluoroethylene oligomer firmly in a schuppen structure. For this reason, a mold-release characteristic and sliding nature are only not only good but excellent in abrasion resistance and a mechanical strength.

[0018] In this invention, since electrostatic powder coating or a surface active agent is made to distribute, and the fine particles of polytetrafluoroethylene oligomer are made liquefied and applied with simple means, such as a brush, and spray spraying or dipping, it can carry out with a simple facility and that work environment gets worse can also use polytetrafluoroethylene oligomer without futility.

[0019]

[Example]

An example of a coating process is shown in [example 1] drawing 2 . In the process S1 which manufactures a base material, a base material is fabricated in a predetermined configuration by machining etc. The base material has the field (metal mold inner surface) which touches matrix resin, such as an epoxy resin, like the iron metal mold for for example, FRP flat spring shaping. The main component of this base material is Fe.

[0020] In the honing process S2 carried out if needed, honing is performed by striking a particle against the fields (for example, metal mold inner surface etc.) which should carry out coating of the base material. By this honing, since much minute irregularity is fabricated by the base material front face, the surface area of a base material increases compared with processing before. However, this honing process S2 can be omitted.

[0021] A base material front face is made to generate the interlayer who consists of a Fe-aluminum intermetallic compound (intermetallic compound by Fe component and Melting aluminum of a base material) by immersing the above-mentioned base material into melting aluminum in the surface treatment process S3. The minute projection of a majority of shape of a scale which consists of a Fe-aluminum intermetallic compound has covered the base material front face without the clearance so that this interlayer may expand to drawing 3 and it may be shown.

[0022] For this reason, since the bonding strength of the minute projection (interlayer) and base material which consist of a Fe-aluminum intermetallic compound is very large while an interlayer's surface area increases by leaps and bounds, the duty which holds firmly the particle of the polytetrafluoroethylene oligomer applied behind in a schuppen structure is achieved. In order that a Fe-aluminum intermetallic compound may be very hard and may show the high degree-of-hardness value of HV1000 by Vickers hardness number, it raises remarkably the abrasion resistance on the front face of a base material. In addition, the thickness of the schuppen structure (interlayer) of the example of a graphic display was about 30 micrometers.

[0023] On the other hand, in coating-material preparation process S4, the liquid (TFEO dispersion liquid) which carried out underwater distribution of the fine particles (particle size of about 4 micrometers) of polytetrafluoroethylene oligomer with the surfactant (Sumitomo 3M and flow lard FC135) etc. is made.

[0024] The above-mentioned TFEO dispersion liquid are applied to an interlayer with proper spreading means, such as brush coating, in the spreading process S5. In addition, you may apply with a spray instead of brush coating, and may apply with simple means, such as dipping (immersion). Or you may make it make the fine particles of polytetrafluoroethylene oligomer adhere to fixed thickness by electrostatic coating.

[0025] suitable [at temperature (for example, 350 degrees C) higher than the melting point (320 degrees C) of polytetrafluoroethylene oligomer] in the printing process S6, after passing through the above-

mentioned spreading process S5 -- it burns by carrying out time amount (for example, 1 hour) heating. Drawing 4 expands the surface state of the coating layer after printing.

[0026] As shown in drawing 4 , after the particle of polytetrafluoroethylene oligomer had entered between the above-mentioned middle class's scale-like minute projections, the particle comrade of polytetrafluoroethylene oligomer fused each other, it combined each other firmly, and the base material front face was thoroughly covered with the polytetrafluoroethylene oligomer layer. An example of the thickness of a polytetrafluoroethylene oligomer layer is about 15-16 micrometers.

[0027] In addition, since much irregularity is formed in the base material front face of honing when the above-mentioned honing process S2 is beforehand carried out on the base material front face, it is expectable to raise the fixed reinforcement of polytetrafluoroethylene oligomer further with the increment in the surface area of the anchor effect and base material.

[0028] When the layered product which has a coating layer by said example was applied to the molding die of an epoxy resin product, even if this metal mold did not apply a release agent, it was able to show the good mold-release characteristic over 500 times or more of resin molding cycles.

[0029] Since a mold-release characteristic is quantified and expressed, the contact angle over water may be measured. Then, this invention persons measured the contact angle over the water of the coating layer obtained according to the above-mentioned example, and the contact angle over the water of the conventional polytetrafluoroethylene plate, and compared both.

[0030] Consequently, as for the contact angle of the coating layer of the layered product of this example, it was proved to the contact angle of a polytetrafluoroethylene plate having been 110 degrees 135 degrees and that it became, a big value was shown and a good mold-release characteristic was shown. This example can demonstrate high endurance while it can demonstrate the outstanding mold-release characteristic in the metal mold for fabricating the strong resin product of adhesive strength like epoxy or urethane since it shows the outstanding water repellence and oil repellency for example.

[0031] After passing through the process S1 which makes a base material, and the honing process S2 performed if needed, the above-mentioned base material is made to vapor-deposit aluminum in thickness of 2 micrometers by sputtering in the surface treatment process S3 in the same coating process (drawing 2) as the [example 2] example 1. after it, a vacuum or Ar, and N2 etc. -- heating of 1 hour is performed in an inert gas ambient atmosphere at the temperature (for example, 800 degrees C) of 500 degrees C - 1000 degrees C, and the intermetallic compound of Fe-aluminum is made to generate on the surface of a base material The other coating process is the same as an example 1. In this way, the minute projection of the shape of a majority of scale has covered the base material front face without the clearance like [the formed interlayer] the Fe-aluminum intermetallic compound of an example 1.

[0032] Other examples of a coating process are shown in [example 3] drawing 5 . In the process S1 which manufactures a base material, a base material is fabricated in a predetermined configuration by machining etc. like said example 1. A base material is the same iron metal mold as an example 1.

[0033] In the honing process S2 carried out if needed, honing is performed by striking a particle against the fields (for example, metal mold inner surface etc.) which should carry out coating of the base material. By this honing, since much minute irregularity is fabricated by the base material front face, the surface area of a base material increases compared with processing before. However, this honing process S2 can be omitted.

[0034] A base material front face is made to generate a phosphoric-acid zinc coat by chemical conversion in the surface treatment process S3. An example of chemical conversion is immersed in the water solution of the 1st phosphoric-acid zinc in iron. The minute projection of a majority of shape of a scale which consists of a phosphoric-acid zinc coat [Zn3 2 (PO4), 4H2 O+Zn2 Fe(PO4)2, and 4H2 O] has covered the base material front face without the clearance so that the interlayer by this chemical conversion may expand to drawing 6 and it may be shown.

[0035] For this reason, since this example also has the very large bonding strength of the minute projection (interlayer) and base material with which an interlayer's surface area consists of a phosphoric-acid zinc coat while increasing by leaps and bounds, it achieves the duty which holds firmly the particle of the polytetrafluoroethylene oligomer applied behind in a schuppen structure. this kind of formation --

in order to show a degree-of-hardness value also with an expensive coat, the abrasion resistance on the front face of a base material is raised remarkably. The thickness of the schuppen structure in this case (interlayer) is presumed to be about 1-3 micrometers.

[0036] In coating-material preparation process S4, the liquid (TFEO dispersion liquid) which carried out underwater distribution of the fine particles (particle size of about 4 micrometers) of polytetrafluoroethylene oligomer with the surfactant like said example 1 is made. These TFEO dispersion liquid are applied with proper spreading means, such as brush coating, a spray, dipping, and electrostatic coating, in the spreading process S5.

[0037] suitable [at temperature (for example, 350 degrees C) higher than the melting point (320 degrees C) of polytetrafluoroethylene oligomer] after it and in the printing process S6 -- it burns by carrying out time amount (for example, 1 hour) heating. Drawing 7 expands the surface state of the coating layer after printing. As shown in this drawing, after the particle of polytetrafluoroethylene oligomer had entered between the above-mentioned middle class's scale-like minute projections, the particle comrade of polytetrafluoroethylene oligomer fused each other, it combined each other firmly, and the base material front face was thoroughly covered in the polytetrafluoroethylene oligomer layer.

[0038] When this example was applied to the molding die of a synthetic-resin product, the good mold-release characteristic was able to be shown over 500 times or more of resin molding cycles, without applying a release agent.

[0039] In order to evaluate the friction wear property of said examples 1-3, wear-resistant trial and measurement of coefficient of friction were performed to drawing 10 using the friction abrasion tester 10 of the pin block system shown notionally. The result is shown in drawing 8 and drawing 9 . A testing machine 10 forces the block 12 with a V groove from the both sides of the cylinder-like test piece 11 which rotates with constant speed (for example, 100rpm), forces it on every fixed time amount (for example, for 1 minute), and makes a load increase gradually. And while pushing with the torque which the revolution took and measuring coefficient of friction from a load, according to too much forcing force, a forcing load when a test piece 11 and block 12 produce seizure is measured, and the friction wear property of a test piece 11 and block 12 is investigated. A test piece 11 is connected with a main shaft 15 by the lock pin 14 made from brass.

[0040] Here, the test piece 11 and the thing which gave the coating layer of said examples 1-3 to the block 12 were compared with the example of a comparison at the time of not preparing a coating layer (unsettled article with a base material) using the test piece 11 which uses a steel type AISI3135 as a base material, and the block 12 which consists of AISI1137, and the friction wear property was investigated. The ambient atmosphere of a part where a test piece 11 and block 12 touched was made into two conditions with the inside of atmospheric air and an oil (dry type) (spindle oil).

[0041] In atmospheric air, an unsettled article (example of a comparison) is burned by about 150 Lbs (es), and coefficient of friction has also become 0.18 or more big values so that the measurement result of the printing load shown in drawing 8 and the measurement result of coefficient of friction shown in drawing 9 may show. On the other hand, a printing load of what gave the coating layer of polytetrafluoroethylene oligomer on the Fe-aluminum intermetallic compound (examples 1 and 2) improves with 700Lbs(es), coefficient of friction is also 0.09 and the quite low value is shown compared with the unsettled article.

[0042] moreover, a printing load of what gave the coating layer of polytetrafluoroethylene oligomer on the phosphoric-acid zinc coat (example 3) improves substantially with 1200 or more Lbses, and coefficient of friction is also 0.06, and it is markedly boiled compared with an unsettled article, and shows the low value.

[0043] Although coefficient of friction at the time of contacting an iron comrade in an oil is generally made about into 0.1, since the layered product in which the coating layer of examples 1-3 was prepared shows coefficient of friction lower than 0.1 also in any in air and an oil, demonstrating the engine performance which was excellent also in the application as moving parts, such as a dry bearing (dry bearing), is expected. By trial in an oil, the printing load of an unsettled article shows 400Lbs(es), and coefficient of friction shows 0.11.

[0044] moreover, into the oil, while 1750Lbs(es) and the printing loads of an example 3 are 1300Lbs (es), and the printing load of examples 1 and 2 is markedly boiled compared with an unsettled article and shows a high value, coefficient of friction serves as 0.06 and 0.075, and a very small value, respectively. Thus, when the lubricating oil was used together in the coating layer of examples 1-3, it was proved that friction / wear property of having excelled dryness further was shown.
[0045] In addition, in the example 3, even if it formed the phosphoric-acid manganese coat instead of the above-mentioned phosphoric-acid zinc coat as an interlayer, friction / wear property almost equivalent to an example 3 was able to be demonstrated. Moreover, in the case of the base material which uses aluminum as a main component like the metal mold made from an aluminum alloy used for foaming of urethane resin etc., the outstanding mold-release characteristic was able to be acquired also by forming much minute irregularity in a base material front face by honing, making surface area increase, and applying and baking the fine particles of the same polytetrafluoroethylene oligomer as said example on it.
[0046]
[Effect of the Invention] Also when according to this invention polytetrafluoroethylene oligomer excellent in a mold-release characteristic and sliding nature can be firmly fixed to a base material front face and it moreover applies to large-sized members, such as metal mold, it is not necessary to use a large-sized facility like a plating tub, and a lot of plating liquid is also unnecessary, and it can carry out safely by low cost. Moreover, the coat of polytetrafluoroethylene oligomer can be easily fixed also to the base material of a complicated configuration firmly, and the mechanical strength is highly excellent in abrasion resistance.

[Translation done.]